ION EXCHANGE AND ABSORPTION TECHNIQUES TO APPLY CATALYSTS FOR LIQUEFACTION OF LOWER RANK COALS

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ABSTRACT

Samples of Beulah-zap lignite, Black Thunder and Wyodak subbituminous, and Illinois #6 high volatile bituminous coals have been prepared by acid treatment to remove exchangeable cations. Subsequent treatments were made with solutions of catalytic metals including iron or cobalt or nickel to exchange with the acid sites, or with molybdate to adsorb on the surface. Samples were then subjected to liquefaction conditions in microautoclave tubular microreactors and solvent extraction was used to establish total conversion or yields of oils, asphaltenes and preasphaltenes. Results of the liquefaction experiments are compared with the catalyst loadings.

INTRODUCTION

The use of catalysts to improve the liquefaction of lower rank coals has a number of advantages. The disadvantages of cost and recovery of these metals has led to a study of methods of application which can place small amounts of metal on the coal to minimize the cost and need for recovery. A variety of techniques have been used for catalyst application, including blending, "incipient wetness", ion exchange and surface adsorption. This paper provides details of some recent work with the ion exchange and surface adsorption techniques and subsequent liquefaction experiments.

An earlier paper (1) has indicated the value of these techniques, and some structural aspects of ion exchange studies as part of the preparation for catalyst loading.

The coal structure of low rank coals is known to contain reactive functional group types including carboxylate and phenolic. The proportion of these groups decreases with increasing rank. The carboxylates are known to be able to act as ion-exchange materials. The functional groups are frequently linked to a variety of alkali and alkaline earth cations. The inorganic cations can be detrimental due to fouling of boilers during operation or reducing yields for liquefaction.

The latter deleterious effects of calcium in the coal (and any other exchangeable cations) can be overcome by removal of these species. A number of studies have indicated that low rank coals can be treated with acids to exchange the cation species with hydrogen ions (2-4). The cations can then be washed away from the coal to minimize their effect. A sulfurous acid treatment will also remove cations and prepare the the samples for ion exchange (5).

EXPERIMENTAL

Ion Exchange - Acid Washing

The samples were a Black Thunder mine (Wyoming) subbituminous coal and the Argonne Premium Beulah-Zap lignite, Wyodak subbituminous, Illinois #6 high volatile bituminous coals (6).

The acid washing treatments involved the three Argonne coal samples. The -20 mesh samples were dry screened to -20+200 mesh. Weighed amounts (about 30 grams) of the screened samples were slurried with deionized water. Fines (still -200 mesh) were decanted away from the slurry using about 200-600 ml of water. The slurry, containing about 15-20 grams of coal, was washed into a special 50 ml burette. The burette had been fitted with a coarse fritted glass disk at the 50 ml mark to retain the coal but allow solutions to pass. Fine coal particles had to be removed to avoid pluggage of the frit. A siphon flow provided a uniform flow of 0.1 N HNO_3 (or H_2SO_4 for some of the Wyodak coal) to the sample. Acid flow rates were typically about 1-3 ml/minute and were set according to the ability of the solution to pass through the coal bed. Following the treatment with the acid, the samples were washed with distilled water fed by the siphon, and the record of pH and ion concentration was obtained in a manner similar to that for the acid treatment. The burette tip was fitted with tubing to connect a flow-through pH electrode from Cole-Parmer, or from Microelectrodes, Inc (Londonderry, NH) and with ion-selective electrodes for Ca^{+2}, Na^+ and K^+. The electrodes were used with an Orion EA940 pH meter. The pH meter in turn was connected to an IBM model AT computer for data acquisition. A program was written which allowed data points to be acquired at specific intervals in the range of 10-18 seconds. The data files were then manipulated with a word processor and Lotus 123 macros to permit plots to be drawn of the data.

For the Beulah-Zap and Illinois #6 coals, the calcite reacted with the acid to produce bubbles of carbon dioxide in the column. These bubbles tended to block the flow of acid. Therefore, an initial acid treatment was given before the burette studies for further samples. The acid wash was followed by a water rinse. Three cycles of acid wash and water rinse were used before the catalysts were added to the coals.

The Black Thunder sample was prepared by blending a large sample and screening to obtain a -8+20 fraction. This material was allowed to contact sulfurous acid for 4 hours. The acid and dissolved mineral matter were filtered and flushed with water. Samples of this treated coal were used for the catalyst loading.

Catalyst Loading

Catalyst materials were added by ion exchange or adsorption techniques. For the addition of Fe, Co or Ni, solutions containing 1000 ppm of metal were made up and added to acid washed coal samples. The solution of ferrous sulfate was acidified slightly to avoid precipitation of hydroxide species. The amount of solution used was twice the desired amount to be added for any of Fe, Co or Ni. This amount was added to the coal slurry, stirred well and allowed to exchange for up to about 42 hours. For the addition of Mo, the procedure developed by Schroeder was used (8). The Mo concentration used was 1500 ppm at a pH of 2. The adsorption is relatively rapid and provided the loadings indicated in Schroeder's procedure. Following reaction with the coal the catalyst solution was washed from the coal with several volumes of distilled or deionized water. The weighed solution was then analyzed for concentrations of the catalyst materials. Catalyst loadings were determined from the difference in the amount of material in the initial and final solutions.

Liquefaction Studies

Initial coal samples (comparing raw, water washed and acid washed) were liquefied in tubular microreactors to establish yields based on THF solubility (total conversion) and heptane solubility (oil yield). Conditions were: solvent 1-Methyl Napthalene (non-donor) , 2:1 solvent:coal; 425 C, 30 minute reaction, cold charge at 1000 psi H2, (1700-1800 hot), reactor volume of about 20 cm^3. The reactor charge was 2g of 1-methylnaphthalene as the reaction solvent and 1.33 g maf coal. Later tests with catalyst-loaded samples included 0.67 g pyrene as a test hydrogenation compound.

For the Wyodak samples, some runs were made with a process-derived solvent, designated V1074, obtained from the Wilsonville, Alabama liquefaction pilot plant. A hydrogen donor solvent, dihydroanthracene (DHA), was also used for comparison.

The products from the liquefaction reactions were removed from the reactor with THF. Conversion of coal to THF solubles was determined. In the initial test the residue solubility in heptane was also determined. For the catalyst-loaded samples The amount of pyrene hydrogenation to hydrogenated products that occurred in the reactions was obtained by gas chromatographic analyses using a Varian Model 3400 equipped with a J&W DB-5 fused silica 30-m column and flame ionization detection.

RESULTS AND DISCUSSION

Ion Exchange

The readings from the electrodes indicated that the coals were washed free of exchangeable cations with the exception of calcium after the first cycle. The calcium came out during the water rinse over a pH range of 1.5-2.5. The possibility of calcium in the clay of the samples is assumed from this data. Additional calcium was removed during the later cycles using either the acid or the rinse water. The final concentrations were micromolar.

Liquefaction Studies

Initial runs were made to compare fresh material from ampules and acid treated Wyodak samples. Samples of the raw coal were compared with both water-washed and acid-washed Wyodak samples. Ash values were also obtained. The water-washed and acid washed samples were dried before the ash determination. The results are summarized below.

Values in %

Coal Sample	moisture	ash	dry ash	reduction
Raw	27.39	6.31	8.69	0
Water washed	6.4	7.81	8.34	4.0
Acid washed	6.96	3.46	3.72	57.2

These microreactor liquefaction results are summarized below.

Raw Sample	THF soluble (total conv.)	Heptane soluble (oil yield)
Raw	55.2,56.1	34
Water Washed	44	27
Acid washed	37	24

The total conversion and oil yields of the three initial samples decreased with the extent of treatment. This effect may be due to the amount of handling, which increases oxidation. The samples were kept under a layer of water to avoid oxidation.

Samples of acid washed Beulah-Zap, Wyodak and Illinois #6 were compared in several solvents.

The results for total conversion are indicated below:

Coal	1 MeNap.	V1074	DHA
Beulah-Zap	73.5	74.1	86.7
Wyodak	71.4	85.9	86.9
Illinois #6	86.4	86.5	86.4

The reaction conditions were: 410°C, 30 min., no catalyst and 1250 psig H_2 introduced at ambient temperature.

The Illinois #6 sample gave consistent relatively high total conversions. This sample had the highest total sulfur content in these coals. For the Wyodak coal the process derived solvent and the hydrogen donor solvent gave very similar total conversions, while the non-hydrogen donor solvent gave lower conversions. For the Beulah-Zap coal, the non-donor solvent and process-derived solvent gave very similar conversions which were less than that obtained with the hydrogen donor solvent, dihydroanthracene (DHA). The DHA gave very similar total conversions with each of the coals. The maf organic sulfur % values for the Illinois #6, Wyodak and Beulah-Zap are: 2.38, 0.47 and 0.70. The pyritic sulfur values are: 2.81, 0.17 and 0.14.

Subsequent catalyst loading produced a series of samples in several batches to give a variety of loadings in the 100-1000 ppm range. These were also run in microautoclave tubing reactors to establish liquefaction yields based on THF solubility (total conversion) and pyrene conversion (catalyst reactivity).

The samples prepared with Ni and Co were run about one month after preparation, and the others about two months after.

The results of duplicate runs are given below:

Sample	1st Cat. Ldg.	2nd Cat. Ldg.	Ave. Coal Conv.	Ave. Pyrene Conv.
Black Thunder				
One catalyst metal				
BT-1-Mo	829		65.5	5.3
BT-1-Fe	548		60.1	3.4
BT-1-Co	212		63.3	2.9
BT-1-Ni	257		64.0	2.6
BT-2-Mo	418		63.3	3.1
BT-2-Fe	483		65.9	3.0
BT-2-Co	83		65.1	2.9
BT-2-Ni	464		66.0	2.9
Two catalyst metals				
Fe-Mo-1	456	210	69.1	5.3
Fe-Mo-2	484	70	66.5	4.8
Fe-Ni-1	408	224	67.5	3.9
Fe-Ni-2	472	106	66.4	4.0
Wyodak Samples				
Wyodak, raw (no washing)	none		71.4	2.0
Wyodak, (nitric acid washed)	none		41.6	3.1
(Sulfuric acid washed)				
WY-Mo	847		74.2	4.5
WY-Fe	552		74.7	3.3
WY-Co	668		53.3	2.5
WY-Ni	822		75.5	3.1

Cobalt was much more difficult to get on the coal than the Fe or Ni. The analyses of metal loadings are good to 10%. Individual determination values ranged up to 4% different from the averages.

For the Black Thunder coal, regardless of the metal type, metal loading or batch, the coal conversion was very similar and ranged for individual determinations from a low of 59% for Fe batch 1 to a high of 70% for Ni batch 2. The coal conversions for the combined metals were slightly higher and less variable than the individual metals. Pyrene conversions tended to be higher for the combined metals than for individual ones.

Wyodak coal which had been acid washed with H_2SO_4, with the exception of the Co treated sample, gave higher coal conversions than the Black Thunder samples. The primary hydrogenation product produced in each reaction was dihydropyrene. The overall conversions do not appear to be as high as reported for a number of other catalyst preparations. The comparison sample of Wyodak which had been acid washed, but with nitric acid, gave substantially lower total conversion. This may reflect the state of oxidation of the coal.

The pyrene conversion, an indicator of hydrogenation activity, was highest for the Mo catalyst preparations.

CONCLUSIONS:

1. Catalytic metals including Fe, Ni and Co as well as Mo can be placed on lower rank coals following an acid wash in a wide range of concentrations.
2. Comparisons of raw, water washed and acid washed subbituminous samples show reduced yields for more significant treatment.

3. The preparations with different catalysts tended to give similar total conversions.
4. Somewhat higher conversions for the Wyodak coal were obtained from samples which had been treated with sulfuric acid to remove exchangeable cations.
5. Conversions were uniformly high with all solvents for the highest rank samples. Lower rank conversions were lower for the non-donor solvent and also, for the lignite, for the process derived solvent.

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